DIDYMIUM SEPARATION FROM LANTHANUM BY SOLVENT EXTRACTION USING 2-ETHYLHEXYLPHOSPHONIC ACID MONO-2-ETHYLHEXYL ESTER AND LACTIC ACID

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Abstract

This article reports the separation of didymium from lanthanum by solvent extraction using 2-ethylhexyl phosphonic acid mono–2–ethyl hexyl ester (HEH(EHP)) as extracting reagent. The aim of the study was to evaluate the effect of lactic acid addition as well as the feed solution pH variation on the didymium separation from lanthanum. We carried out batch and continuous extraction experiments. In batch experiments, we observed that the extractions of REEs increased along with the increase of lactic acid concentration and feed solution pH. The best conditions for Pr/La separation were obtained at pH 3.5 and lactic concentrations varying between 1.1 and 2.6 times the total REE molar concentration. In the continuous extraction experiments, when no lactic acid was added in the feed solution and with A/O 1:1, the extractions of La, Pr and Nd were 2.0%, 22.3% and 29.5%, respectively. When lactic acid was added in the feed solution, the extractions of La, Pr and Nd were 7.0%, 57.8% and 73.7%, respectively. The addition of lactic acid in the feed solution increased the REE total concentration in the loaded organic phase, the Pr/La separation factor and the total REE mass flow rate, by 2.6, 2.8 and 2.7 times, respectively.

Keywords: Solvent extraction; Rare earth elements; Lactic acid; HEH(EHP).

SEPARAÇÃO DE DIDIMIO E LANTÂNIO A PARTIR DA EXTRAÇÃO POR SOLVENTES USANDO ÉSTER MONO-2-ETIL-HEXÍLICO DO ÁCIDO 2-ETIL-HEXIL FOSFÔNICO E ÁCIDO LÁCTICO

Resumo

Neste trabalho estudamos a separação de dídimo e lantânio utilizando a técnica de extração por solventes e com o extratante éster mono-2-etil-hexílico do ácido 2-etil-hexil fosfônico (HEH(EHP)). O objetivo deste trabalho foi avaliar o efeito que sobre a separação de didímio e lantânio tem a adição de ácido lático e a variação do pH da alimentação aquosa. Realizamos ensaios em batelada e em regime contínuo. Nos testes em batelada, observamos que o aumento da concentração do ácido láctico e do pH aumentaram a extração dos ETRs. As melhores condições de separação de Pr/La foram obtidas em pH 3,5 e ácido láctico em concentração de 1,1 a 2,6 vezes a concentração de ETRs. Em regime contínuo, para uma razão de fases A/O 1:1 e quando o licor não foi condicionado com ácido lático, as extrações de La, Pr e Nd foram: 2,0%, 22,3% e 29,5%, respectivamente. Quando o licor foi condicionado com ácido lático as extrações de La, Pr e Nd foram: 7,0%, 57,8% e 73,7%, respectivamente. A adição de ácido lático na alimentação aumentou a concentração total de ETRs na fase orgânica carregada, o fator de separação Pr/La e a vazão mássica total de ETRs em 2,6, 2,8 e 2,7 vezes, respectivamente, quando se compara com o teste sem a presença do ácido lático na alimentação.

Palavras-chave: Extração por solventes; Elementos de terras raras; Ácido lático; HEH(EHP).

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1 INTRODUCTION

Liquid-liquid separation or solvent extraction is one of the key techniques for separating, purifying and recovering metals on an industrial scale, including rare earth elements [1].

Although saponification of the extractants improves the separation of REEs, this practice poses problems from an environmental point of view, because of the production of wastewater containing ammonia or sodium, which need to be removed before discharging the effluent into the environment.

Several complexing agents have been used to assist in the separation of lanthanides e.g., thiocyanate ion, glycine, 2-ethyl-2-hydroxy butyric acid, 3-mercapto propionic acid, ethylenediamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), lactic acid and acetic acid [2-8]. The thiocyanate ions form complexes with lanthanides with negative charge, which disfavors the extraction of the complex by the cationic extractant di-(2-ethylhexyl) phosphoric acid (D_2EHPA).

The addition of SCN^- favored the separation of the rare earth elements because the constants of stability of the SCN^- - lanthanide complexes decreased as the atomic numbers of the lanthanides increased and the constants of stability of the lanthanide complexes with D_2EHPA increased as the atomic number of the lanthanides increased [2].

Bhattacharyya and Ganguly [3-5] studied the influence of the complexants glycine, 2-ethyl-2-hydroxy butyric acid and 3-mercapto propionic acid on lanthanide separation by the extractant D_2EHPA. Glycine was the only complexing agent capable of increasing the separation of lanthanides when extraction occurred at high acid concentration [3].

The REE separation with the extractant s-nonylphenoxy acetic acid, in the presence of the chelating agent ethylenediaminetetraacetic acid (EDTA), reverses the order of extraction of metals by the extractant D_2EHPA [6]. The stability constant of the complex REE-EDTA increases with increasing atomic number of these elements. The REE-EDTA complex is inactive for the extraction with cationic extractants and only the free REE ions can take part in the extraction. Consequently, yttrium is extracted preferentially from a mixture of heavy rare earths composed of Y, Ho, Er, Tm, Yb and Lu. However, these complexing agents are expensive and difficult to recycle [6].

The addition of lactic, citric and acetic acids to improve REE separation has been studied [7,8]. The separation factors between light rare earth elements were higher when the lactic acid was present in the feed solution than when it was not, under the same conditions [7]. These hydroxy carboxylic acids are weak acids that ionize partially in water. The conjugated base of these acids acts as a pH buffer of the aqueous solution, avoiding drastic decreases of pH and favoring extraction and separation of REEs [8].

The aim of this study was to evaluate, in batch experiments, the influence of feed solution pH and lactic acid concentration on lanthanum separation from didymium (mixture of the elements Pr and Nd). In addition, we assessed, in continuous extraction experiments, the influence of the ratio of the aqueous volumetric flow rate to the organic volumetric flow rate and the addition of lactic acid to the feed solution on lanthanum separation from didymium.

2 METHODS

2.1 Reagents

The extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP)) was purchased from Aodachem (China). The extractant was used without any further purification. Isoparaffin 17/21 was used as a diluent and was purchased from Ypiranga (Brazil). Lanthanum, praseodymium and neodymium oxides (99.9%) were purchased from Pacific Industrial Development Corporation.

The aqueous feed solution of rare earths was prepared by digesting the corresponding rare earth oxide in concentrated hydrochloric acid. The synthetic solution composition was similar to the leach liquor of monazite sand from Brazil and its composition in g L^{-1} was: La_2O_3 — 20.3, Pr_6O_{11} — 4.7 and Nd_2O_3 — 16.3. The total rare earth elements' molar concentration in the feed solution was 0.249 mol L^{-1}. All other chemicals had analytical grade.

2.2 Batch Tests

HEH(EHP) at 0.6 mol L^{-1} was used in all the extraction experiments. General extraction batch experiments were conducted at room temperature by contacting equal volumes (20 mL) of the aqueous and organic phases for 15 min (initial experiments showed that equilibrium was achieved within 5 min). After the separation of the two phases, the rare earth metal contents in the aqueous phase were determined. The feed solution's lactic acid concentration varied between 0 and 3 times the total REE molar concentration. The feed solution pH values investigated were 0.5, 2.0 and 3.5.

2.3 Continuous Runs

The best conditions obtained in the batch experiments were applied in continuous liquid-liquid extraction experiments. Light rare earth element extraction occurred in 10 continuous countercurrent stages. We did not carry out a scrubbing stage of the loaded organic phase. All the experiments were performed in triplicate and the means and standard deviations of all variables were calculated.

Table 1 shows the volumetric flow rates of the aqueous feed solution (A) and organic solutions (O) assessed.

2.4 Chemical Analysis

We determined the Pr and Nd concentrations in aqueous phase by UV-Vis spectrometry (HACH DR 6000 spectrophotometer) and the total REE concentration by

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complexometric titration with EDTA and xylenol orange as indicator. The La concentration was calculated by the difference between the total concentration of REEs and Pr + Nd concentrations.

2.5 Parameter Equations

The accumulated extraction (%E_M) of REEs was calculated from Equation 1 and the metal concentrations in the loaded organic phase were calculated by Equation 2. The total REE concentration in the organic phase is the sum of individual REE concentrations (Equation 3). The distribution ratio of each element (D) is the ratio of the concentration of metal in the organic phase and aqueous phase at equilibrium (Equation 4). The separation factor (β) indicates the degree of separation of two elements and was calculated from the distribution coefficient of two different metals (Equation 5). Finally, we determined the didymium purity in the loaded organic phase and mass flow rate ($\dot{m}_i$) of each element by the Equations 6 and 7, respectively.

$$E_M = \frac{[M]\,\text{feed} - [M]\,N(a)}{[M]\,\text{feed}} \times 100\% \qquad (1)$$

$$[M]_{loaded(o)} = \frac{A}{O}\left([M]_{feed} - [M]_{raffinate(a)}\right) \qquad (2)$$

$$[M]_{total(o)} = \sum [M]_{loaded(o)} \qquad (3)$$

$$D = \frac{[M]_{loaded(o)}}{[M]_{raffinate(a)}} \qquad (4)$$

$$\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}} \qquad (5)$$

$$\%Didymium\ purity = \frac{[Pr]loaded(o) + [Nd]loaded(o)}{[M]_{total(o)}} \times 100 \qquad (6)$$

$$\dot{m}_i = [M]_{loaded(o)} \times O \qquad (7)$$

In these equations, $[M]_{feed}$ represents the REE concentration in the feed solution, $[M]_{Raffinate(a)}$ is the REE concentration in the outlet aqueous solution, $[M]_{loaded(o)}$ is the

Table 1. Volumetric flow rates of aqueous (A) and organic (O) phase solutions assessed in continuous solvent extraction experiments

A/O	Aqueous solution volumetric flow rate (mL min⁻¹)	Organic solution volumetric flow rate (mL min⁻¹)
2:3	20	30
1:1	30	30
3:2	30	20
3:1	30	10

REE concentration in the loaded organic solution, $[M]_{N(a)}$ is the aqueous phase REE concentration in the $Nth-$ cell, and $[M]_{total(o)}$ is the total REE concentration in the organic phase.

3 RESULTS AND DISCUSSION

3.1 Batch Tests

The results of the solvent extraction process with 0.6 mol L⁻¹ HEH(EHP) for the separation of didymium from lanthanum at different initial pH values are shown in Figure 1.

The extraction of the light REEs increased with rising feed solution pH values and lactic acid concentrations. The overall extraction of REEs from aqueous media by cation exchange extractants can generally be expressed as follows (Equation 8):

$$REE^{3+}_{(a)} + 3H_2A_{2(o)} = REE(HA_2)_3 + 3H^+_{(a)} \qquad (8)$$
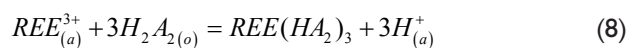
The organophosphorus acid extractant (H_2A_2) exchanges protons with the REE ions present in the aqueous phase. The extraction of REEs causes an increase in the aqueous phase acidity.

The pKa value of lactic acid is 3.86 and when the feed solution initial pH increased, the extension of the lactic acid (HLa) ionization and consequently the lactate ion (La⁻) concentration in the solution also increased (Equation 9). At pH 3.5, the lactic acid was 33% ionized. In the aqueous solution, the lactate ions combine with hydrogen ions released by the organic extractant. Therefore, the lactate ions prevent the acidity of the aqueous solution from increasing drastically, improving the extraction and separation of the rare earth elements (Equation 10).

When initial pH and lactic acid concentration of the feed solution increased, the equilibrium pH of the raffinate also increased, and consequently the extraction reaction was shifted toward formation of more products and higher extractions.

$$HLa_{(a)} = La^-_{(a)} + H^+_{(a)} \qquad (9)$$

$$H^+_{(a)} + La^-_{(a)} = HLa \qquad (10)$$

The selectivity of the extractant regarding Nd and Pr is clearly indicated. The enhancement of the extraction from La to Nd is explained by the difference in the acidity of these elements, which increases from La to Lu. The difference in acidity is related to a decrease in the ionic radii of the REEs with the increase of the atomic number in the lanthanide series, known as lanthanide contraction. The very low extraction of La helps separation of this rare earth from the mixture.

The separation factors $\beta_{Pr/La}$, $\beta_{Nd/La}$ and $\beta_{Didymium/La}$ in the extraction for the different pH values are shown in Figure 1. The highest separation factors were obtained at feed solution pH 3.5. At this pH, the separation factors

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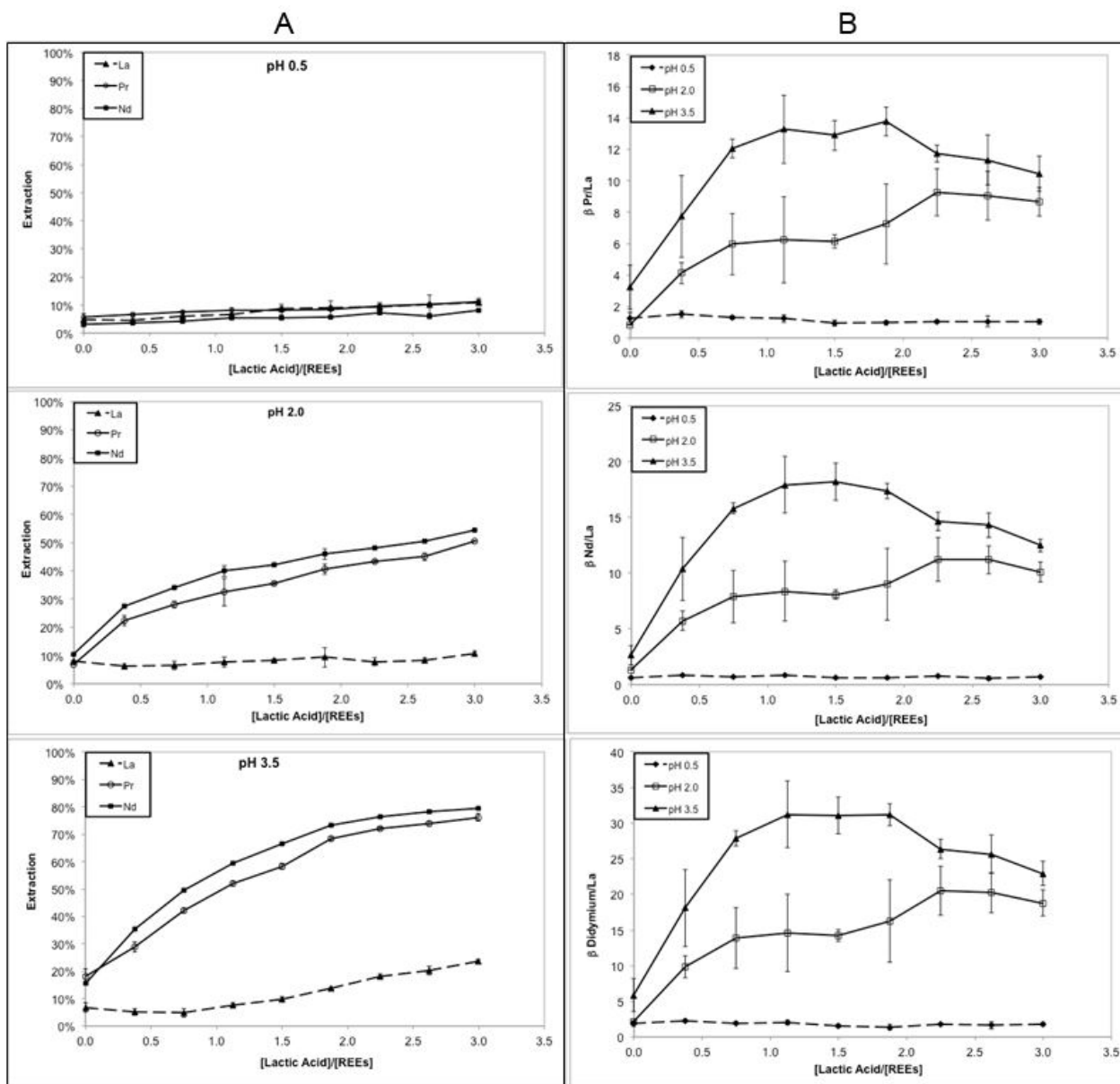
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Figure 1. (A) Effect of lactic acid concentration and feed solution pH on the extraction of light REE s. (B) Effect of lactic acid concentration and feed solution pH on the separation factors: $\beta_{Pr/La}$, $\beta_{Nd/La}$, $\beta_{Didymium/La}$.

increased when the lactic acid concentration increased from 0 to [Lactic acid]/[REE] = 0.7 and afterward remained at the same level until [Lactic acid]/[REE] = 1.9 and subsequently decreased with increasing lactic acid concentration, due to co-extraction of La. The higher lanthanum extraction increment than praseodymium and neodymium extraction increments when the [Lactic acid]/[REE] > 1.9 is the result of the high equilibrium pH and high lanthanum aqueous concentration (Figure 2). At pH 2.0, the separation factors increased when the lactic acid concentration increased in all lactic acid concentration ranges studied. At this condition, the equilibrium pH was lower than when the feed solution initial pH was 3.5, resulting in higher neodymium and praseodymium extraction increments than in the lanthanum

extraction increment when the lactic acid concentration increased (Figures 1 and 2).

3.2 Continuous Runs

We also investigated the influence of A/O ratio on the extraction and separation of didymium from lanthanum in continuous experiments when no lactic acid was added to the feed and when lactic acid was added at concentration of 0.26 mol L^{-1} ([lactic acid]/[REEs] = 1.1). Generally, the extraction of the elements decreases when the A/O ratio increases, probably because the lower availability of the organic solvent.

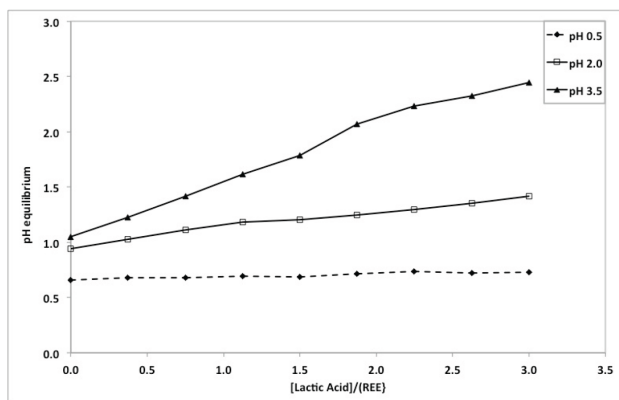At the three different A/O ratios, the extractions of the REEs had the following order: Nd > Pr > La, as is

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Figure 2. Equilibrium pH of the raffinate solution obtained for various feed solution initial pH values and lactic acid concentrations.

depicted in Figure 3. The selectivity of the extractant with respect to Nd and Pr is clearly indicated.

It can be seen that the extractions of all REEs increased significantly when lactic acid was present in the feed solution in comparison with the extractions without adding lactic acid (Figure 3).

In spite of the lesser REE extraction when the A/O ratio increased, the concentration of REEs in the organic phase increased as a result of decreasing the organic phase volume flow rate, augmenting the concentration of the elements in the organic phase.

The highest values of $\beta_{Pr/La}$ and didymium purity were obtained when the A/O was equal to 1:1, whether or not lactic acid was present in the feed solution.
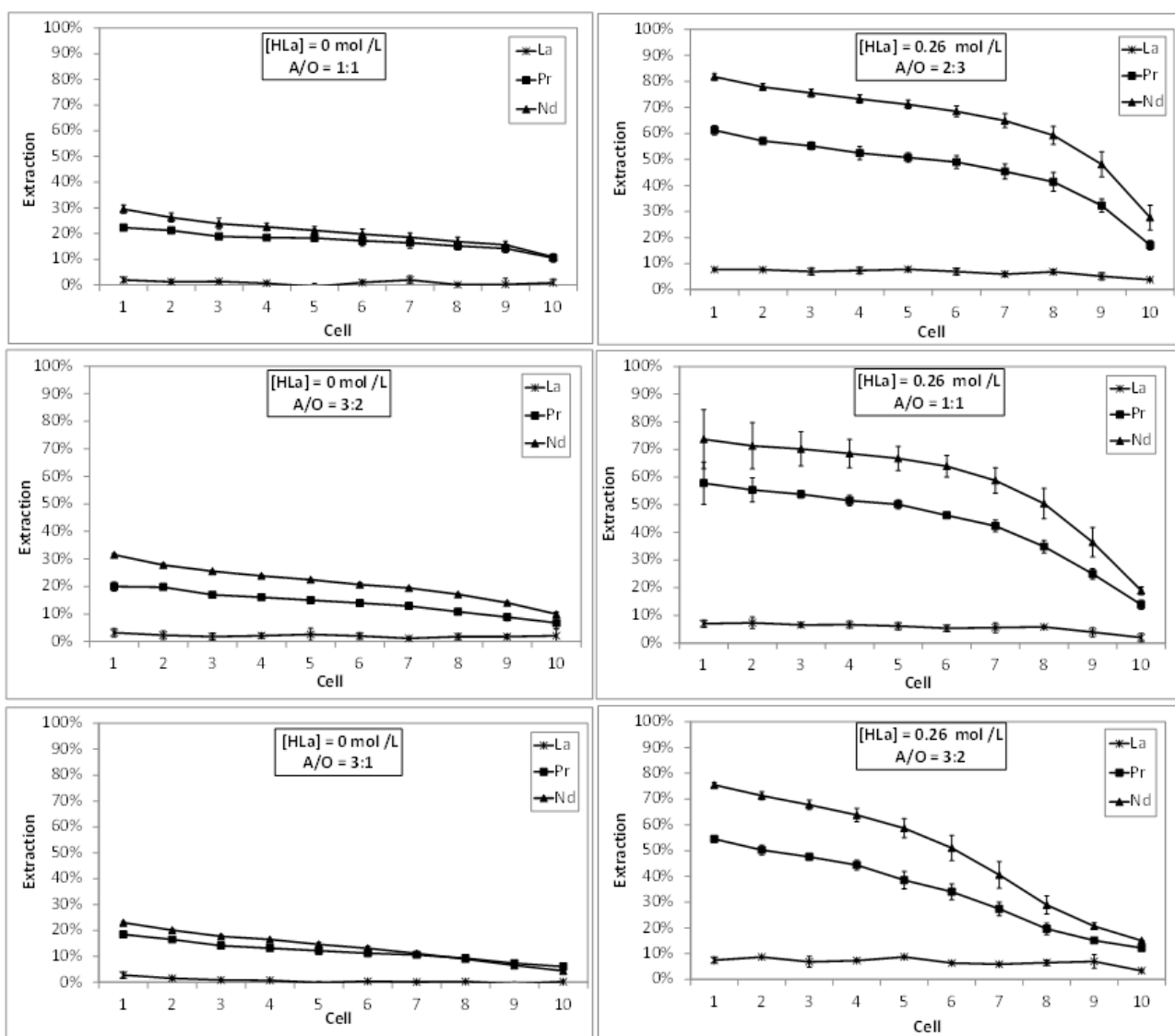

Figure 3. Cumulative extractions of rare earth elements obtained by different A/O ratios when no lactic acid was added in the feed solution and when lactic acid was added (0.26 mol L^{-1} or [HLa]/[REEs] = 1.1). [HLa] = lactic acid concentration in the feed solution.

The REE concentrations in the loaded organic solution, the separation factor between La and Pr, the didymium purity and the total mass flow rate were higher when the feed solution was doped with lactic acid compared to the results obtained without lactic acid, at the same A/O ratio.

For example, when the A/O ratio was 1:1, the total REE concentration and total mass flow rate augmented by 2.6 and 2.7 times when lactic acid was added in the feed solution, in comparison with the results obtained without lactic acid (Tables 2 and 3).

When the feed solution was free of lactic acid, the highest values of $\beta_{Pr/La}$ and didymium purity, obtained when the A/O ratio was 1:1, were 10.7 and 91.0%, respectively (Table 2). When lactic acid was added in the feed solution, the highest values of $\beta_{Pr/La}$ and didymium were 29.9 and 92.0%, respectively, also obtained when the A/O ratio was 1:1 (Table 3). The addition of lactic acid did not increase the didymium purity obtained in continuous runs,

but the addition of lactic acid increased the $\beta_{Pr/La}$ and mass flow rate of the REEs.

A disadvantage of adding lactic acid is the increase of organic matter concentration in the wastewater. Thus, before the discharge of wastewater it is necessary to remove the lactic acid from the aqueous solution by solvent extraction with TBP or removal by biological treatment [7].

It is possible to observe that when lactic acid was not present in the extraction system, the total mass flow rate was reduced when the A/O ratio increased from 1:1 to 3:1. When the feed was conditioned with lactic acid, the total mass flow rates first increased when the A/O changed from 2:3 to 1:1 and afterward decreased when the A/O changed from 1:1 to 3:2. The Pr, Nd and total mass flow rates were the highest when the A/O was 1:1 when the feed solution was free of lactic acid and conditioned with lactic acid.

Some previous studies have reported the separation of light rare earth elements in continuous regime [9-11].

Table 2. Effect of A/O ratio on the extraction and separation of REEs obtained in continuous extraction experiments when the feed was lactic acid free

A/O	[REE] loaded organic (g L^{-1})	$\beta_{Pr/La}$	Didymium purity (%)	Mass Flow Rate (mg min^{-1})
1:1	La = 0.44 ± 0.21	10.7 ± 1.3	91.0 ± 1.2	La = 16.8 ± 1.4
	Pr = 1.08 ± 0.04			Pr = 32.4 ± 1.3
	Nd = 4.75 ± 0.3			Nd = 142.4 ± 7.7
	Total = 6.28 ± 0.28			Total = 188.3 ± 8.5
3:2	La = 1.2 ± 0.3	7.7 ± 0.4	87.3 ± 2.9	La = 24.2 ± 5.8
	Pr = 1.3 ± 0.1			Pr = 25.5 ± 2.1
	Nd = 7.00 ± 0.08			Nd = 140.4 ± 1.7
	Total = 9.3 ± 0.4			Total = 189.9 ± 2.5
3:1	La = 2.1 ± 0.6	10.7 ± 3.6	86.4 ± 3.6	La = 21.1 ± 6.2
	Pr = 2.58 ±0.04			Pr = 25.8 ± 0.4
	Nd = 10.7 ± 0.2			Nd = 106.9 ± 1.8
	Total = 15.0 ± 0.7			Total = 154.4 ± 4.3

Table 3. Effect of A/O ratio on the extraction and separation of REEs obtained in continuous extraction experiments with feed solution containing 0.26 mol L^{-1} lactic acid ([HLa]/[REEs] = 1.1)

A/O	[REE] loaded organic (g L^{-1})	$\beta_{Pr/La}$	Didymium purity (%)	Mass Flow Rate (mg min^{-1})
2:3	La = 1.05 ± 0.05	19.0 ± 2.0	90.9 ± 0.4	La = 31.6 ± 1.4
	Pr = 1.7 ± 0.03			Pr = 50.9 ± 0.9
	Nd = 8.79 ± 0.02			Nd = 263.7 ± 0.6
	Total = 11.54 ± 0.02			Total = 346.2 ± 1.1
1:1	La = 1.3 ± 0.3	29.9 ± 1.5	92.0 ± 1.6	La = 39.9 ± 7.9
	Pr = 2.57 ± 0.05			Pr = 77.1 ± 1.4
	Nd = 12.8 ± 0.2			Nd = 383.2 ± 6.8
	Total = 16.67 ± 0.01			Total = 500.2 ± 0.3
3:2	La = 2.3 ± 0.4	14.9 ± 1.9	90.2 ± 1.3	La = 46.6 ± 7.6
	Pr = 3.3 ± 0.1			Pr = 66.1 ± 1.4
	Nd = 18.0 ± 0.2			Nd = 360.8 ± 4.4
	Total = 23.7 ± 0.7			Total = 473.5 ± 13.3

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Nair and Smutz [9] reported the separation of light REEs in 10 extraction stages with D$_2$EHPA 1 mol L^{-1} and 4 stages of scrubbing with HCl 0.5 mol L^{-1}. The authors obtained 99.8% pure lanthanum in raffinate and 28% lanthanum, < 2% cerium, 15.8% praseodymium, 53% neodymium and <1% samarium in the organic phase.

In a process developed by Narayanan et al. [10], Nd$_2$O$_3$ with 99% purity was obtained from feed solution containing Nd, Pr, Ce and La by solvent extraction with 1.0 mol L^{-1} HEH(EHP) partially saponified. The aqueous feed solution was brought in contact with the extractant in 18 stages. The loaded organic phase, containing mainly Nd and Pr, was washed in 60 stages with a slightly acidic and diluted solution of neodymium chloride. Most co-extracted Pr, Ce and La were removed in this scrubbing step from the organic phase and mixed with the aqueous feed. The Nd present in the loaded organic phase passed through 6 stages of stripping with dilute HCl. Thereafter; the organic extractant was regenerated with concentrated HCl and sent back to the extraction process. Nd was precipitated as oxalate and calcined.

In another process, developed by Morais and Ciminelli [11], La and didymium were separated and La was obtained with 99% purity. The processing consisted of the extraction of REEs with 1.5 mol L^{-1} solution of HEH(EHP) diluted in kerosene in 8 countercurrent stages, followed by scrubbing with 0.25 mo L^{-1} of HCl in 8 stages and stripping with 1 mol L^{-1} hydrochloric acid in 6 stages.

The product purities obtained in the above mentioned studies are higher than the didymium purity obtained in our study, but a larger number of stages and scrubbing steps of loaded organic phase were carried out aiming to increase the purity of the products obtained. In future studies we will investigate the scrubbing of the loaded organic phase in order to increase the didymium purity.

4 CONCLUSIONS

In the present study we carried out batch and in continuous counter-current solvent extraction experiments using HEH(EHP) as extracting reagent and conditioned the feed solution with lactic acid, a weak acid. In the batch experiments, we evaluated the influence of lactic acid concentration and feed solution pH. We observed that when the lactic acid concentration and pH in the feed solution increased, the REE extraction also increased. We defined from batch experiments the feed solution pH and lactic acid concentration that allowed the best La and Pr separation. In continuous extraction experiments, we assessed the influence of A/O ratio on light REE extraction and separation. The experiments revealed that REE extraction diminished when the A/O ratio increased. Furthermore, the presence of lactic acid caused a smaller reduction of aqueous phase pH, enhancing the extraction and separation of light rare earth elements. Nonetheless, to guarantee the buffering effectiveness, the lactic acid must be in solution as a conjugate base. These experiments demonstrated that the use of lactic acid can be a viable alternative to the practice of saponification used in REE separation by the solvent extraction technique.

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